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(54) **Ultrasonic stand-off unit**

(57) Ultrasonic stand off unit fabricated from a polyurethane rubber and having an attenuation of ultrasonic radiation of frequency 2MHz of from 0.5 to 4.0 dB/cm and an acoustic impedance of from 1.45 to 1.6 M Rayls. The unit preferably has a hardness of from 15—50 IRHD and is substantially inert to paraffin and silicone lubricants. It may also be transparent.

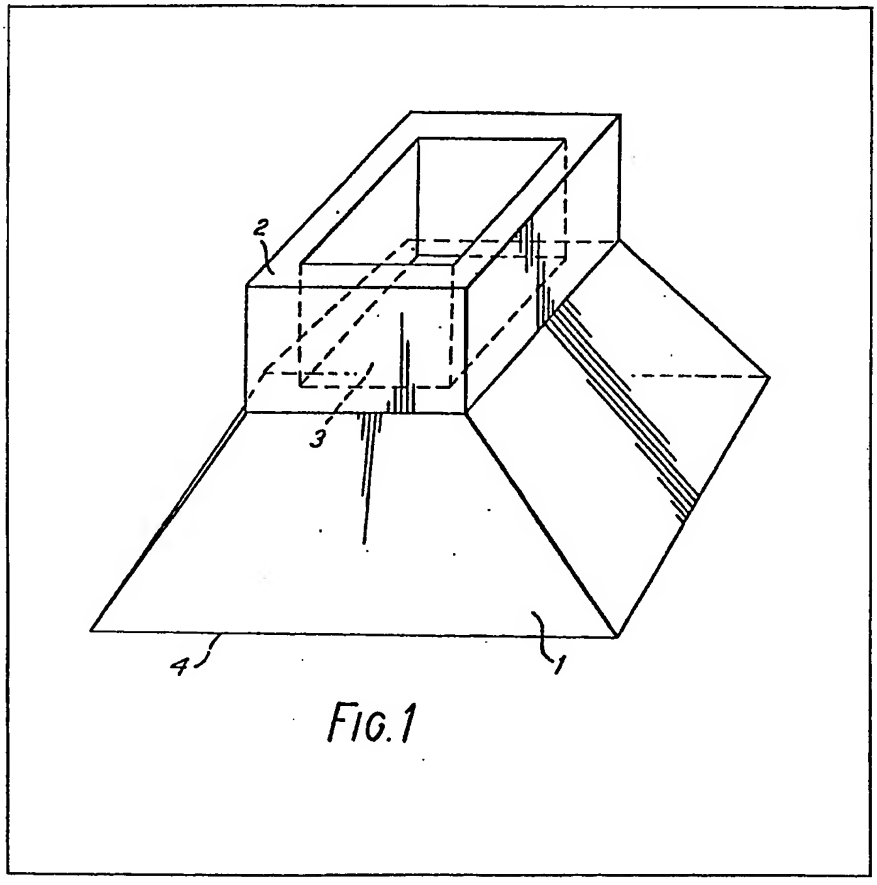

FIG. 1

The drawing originally filed was informal and the print here reproduced is taken from a later filed formal copy.

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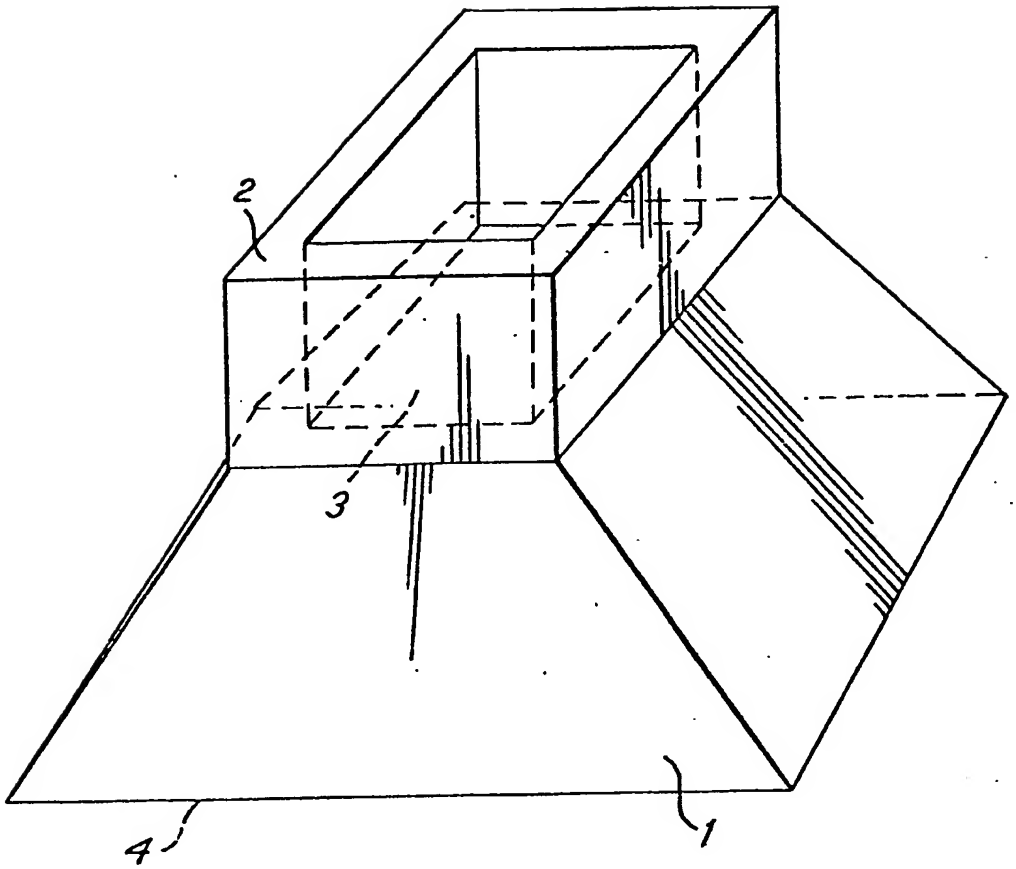

FIG.1

SPECIFICATION

Ultrasonic stand-off unit

This invention relates to an ultrasonic stand-off unit. In the operation of ultrasonic diagnostic apparatus it is necessary to provide an efficient means whereby the ultrasonic radiation generated by the apparatus is transmitted to the object being examined which is normally, of course, the body of the patient. It is necessary that this means, normally referred to as a stand-off unit, should form a close contact with the body, aided if necessary by a lubricant such as paraffin or silicone grease and thus it is desirable that the means be sufficiently resilient to conform to the body contours and preferably also should be chemically resistant to the lubricant required. In addition, and most importantly, the means must be fabricated from a material which does not unduly attenuate the ultrasonic radiation, which is normally of a frequency in the region of 2MHz.

It is an object of the present invention to provide a stand-off unit which satisfies the above criteria.

Accordingly we provide an ultrasonic stand-off unit fabricated from a polyurethane rubber and having an attenuation of ultrasonic radiation of frequency 2MHz of from 0.5 to 4.0 dB/cm and an acoustic impedance of from 1.45 to 1.6 M Rayls. Preferably the unit has a hardness of from 15 to 50 IRHD, more preferably from 30 to 50 IRHD, and is substantially inert to paraffin and silicone lubricants. It is also desirable, for ease of operation, that the unit be optically substantially transparent, although a suitable colouring may in certain instances be included.

Units having an attenuation of from 2.0 to 3.0 dB/cm can conveniently be prepared, as hereinafter described in certain of the specific examples.

We have found that a particularly suitable polyurethane rubber is that formed by the reaction of a polyether polyol having high molecular weight segments between the functional hydroxyl groups and a diisocyanate. Suitable polyether polyols which satisfy this condition include certain polyoxypropylene glycols of molecular weight between 3500 and 6000, and having a chemical structure such that the ratio of molecular weight to hydroxyl number is at least 90.

The reaction between the polyether polyols and the diisocyanate (toluene diisocyanate and isophorone diisocyante are preferred) may take the form of a 'one shot' process in which stoichimetric or near stoichimetric quantities of the reactants are used to produce the required product directly or, alternatively, the polyether polyol may first be reacted with an excess of diisocyanate to form a prepolymer which is then reacted with a further quantity of the polyether polyol sufficient to react with the remaining unreacted isocyanate groups. It has been found to be particularly convenient to prepare a prepolymer containing from 3.5% to 5.0% by weight of unreacted isoycanate groups. The exact percentage may be determined for any particular prepolymer by standard methods e.g. by reacting the prepolymer with an amine such as di-n-butylamine and back titrating the excess amine with hydrochloric acid. These reactions, particularly the reaction of the prepolymer with further polyether polyol may be catalysed; we have found that 1,4-diazobicyclo-(2,2,2)-octane, stannous octoate, N-methyl morpholine and dibutyl tin dilaurate are particularly suitable catalysts. We have found that where it is preferred to keep the temperature of the material low, i.e. not above 40°C, during the reaction of prepolymer and polyether polyol, dibutyl tin dilaurate in a concentration of from 1.2% to 2.1% by weight of total reactants is particularly useful.

The unit of our invention may be in any suitable form including a strip of slab of polyurethane rubber, which should of course be substantially uniform in texture and include no voids since these lead to a marked increase in attenuation. A plasticiser may be incorporated such as n-butyl phthalate. The amount of plasticiser used may vary over a wide range from 0.5% to 60% of the total weight of the plasticised product. Conveniently the unit includes a portion which is shaped by suitable casting or molding to fit closely over the head of the apparatus which is the source of the ultrasonic radiation. In certain designs where the array of elements from which the ultrasonic radiation is produced is recessed into the head it is convenient to fill this recess with material according to the present invention to present a surface which is flush with the rest of the head. In such a case it is particularly preferred to mould the material into the recess by forming it, in situ, using a low temperature (40°C) polymerisation process from the prepolymer and polyether polyol. To give added protection from mechanical damage and possible moisture absorption a PVDF film of thickness from 10^{-3} to 2.10^{-3} inches may be applied over this insert.

In one form, as illustrated in the accompanying drawing wherein Figure 1 is a perspective view of a stand-off unit the unit comprises an integral one-piece moulding of polyurethane rubber in which a lower diverging portion, 1 is surmounted by a portion of rectangular section which defines a rectangular opening 3 into which fits the working head of an ultrasonic generator, which head conveniently contains an array of transducers. The precise geometrical shape of the stand-off unit may be modified for example as described and claimed in our copending application no. 48918/77 wherein the input face, 3, and the output face 4 are inclined to one another at an angle such that reflected waves components from different parts of the output face interfere destructively and/or as in our co-pending application no. 53110/77 wherein the output face, 4, is corrugated.

Optionally, to afford mechanical protection to the boot and in particular to the rectangular opening 3 which may be subjected to significant wear when the head of the ultrasonic generator is inserted or

removed therefrom, at least the side walls of this opening may be coated e.g. by dip coating with a thin layer (about 10^{-3} inches) of a mechanically stronger polymeric material e.g. a more cross-linked polyurethane.

The preparation of a number of polyurethane rubber compositions suitable for production of the stand-off units of the invention will now be illustrated by the following Examples. It will be understood that the invention is in no way limited to particular embodiments described therein.

EXAMPLE 1

A polyoxypropylene glycol of molecular weight 5300 and hydroxyl number 32

$$\left(\frac{\text{molecular weight}}{\text{hydroxyl number}} = 166\right)$$

was used as the starting material in the following reactions. For convenience this starting material will be referred to as T32/75, this being the code number under which it is commercially available (from I.C.I. Limited). T32/75 (50g.), toluene diisocyanate (2.7g) and, as catalyst, N-methyl morpholine (0.15g) were mixed, degassed and placed in an oven at 100°C for 16 hours. The resultant polyurethane rubber had an impedance of 1.48 M Rayl, an attenuation of 2MHz radiation of 3.5 dB/cm and a hardness of 32 IRHD.

EXAMPLE 2

The procedure of Example 1 was repeated using as catalyst 1,4-diazobicyclo-(2,2,2)-octane (0.025g) to yield a polyurethane rubber of impedance 1.48 M Rayl, an attenuation of 2 MHz radiation of 2.6 dB/cm and a hardness of 33 IRHD.

EXAMPLE 3

(a) T32/75 (11.5g), isophorone diisocyanate (0.8g),n-butyl phthalate (12.3g) and, as catalyst, stannous octoate (0.01g) were mixed, degassed and placed in an oven at 100°C for 1.5 hours. The resultant 50% plasticised polyurethane rubber which was very soft and floppy had an impedance of 1.50 M Rayl and an attenuation of 2MHz radiation of 0.6 dB/cm.

(b) The procedure of Example 3(a) was repeated using the different amounts of n-butyl phthalate plasticiser as set out in the following table to give materials which had the values of impedance and attenuation as also set out in the table.

Amount of n-butyl phthalate		Impedance M. Rayl	Attenuation of 2MHz Radiation (dB/cm)
Weight (g)	% by weight of final product		
8.2	40	1.58	1.1
1.4	10	1.61	1.8
3.1	20	1.55	1.8
5.3	30	1.58	1.3
18.5	60	1.50	0.8

EXAMPLE 4

To toluene diisocyanate (82g) under nitrogen and stirred at 80°C was added over one hour T32/75 (500g) and then the mixture heated whilst continuing to stir to 120°C for 15 minutes. The resultant prepolymer was used in the following procedures (a) and (b).

(a) Prepolymer (100g), T32/75 (200g) and, as catalyst, 1,4-diazobicyclo-(2,2,2)-octane (0.1g) were heated for 16 hours at 100°C to yield a polyurethane rubber having an impedance of 1.50 M Rayl and an attenuation of 2MHz radiation of 2.5 dB/cm.

(b) Prepolymer (100g), T32/75 (200g) and, as catalyst, dibutyl tin dilaurate (0.2g) was heated for 1 hour at 100°C and 16 hours at 40°C to yield a polyurethane rubber having an impedance of about 1.50 M Rayl, an attenuation of 2 MHz radiation of 3.2 dB/cm and a hardness of 28 IRHD. Repetition of this experiment using a curing cycle of 16 hours at 40°C (i.e. omitting the 1 hour at 100°C) yielded a rubber of slightly less attenuation of 3.1 dB/cm.

EXAMPLE 5

To isophorone diisocyanate (105g) under nitrogen and stirred at 80°C was added over one hour T32/75 (500g) and then the mixture heated whilst continuing to stir to 120°C for 15 minutes. This product contained 4.1% free NCO content. The resultant prepolymer was used in the following procedures (a), (b) and (c).

(a) Prepolymer (100g), T32/75 (200g) and, as catalyst, 1,4-diazobicyclo-(2,2,2)-octane (0.1g) were heated for 16 hours at 100°C to yield a polyurethane rubber having an impedance of about 1.50 M Rayl, an attenuation of 2MHz radiation of 2.3 dB/cm and a hardness of 16 IRHD.

(b) Prepolymer (100g), T32/75 (200g) and, as catalyst, dibutyl tin dilaurate (0.2g) were heated for 1 hour at 100°C and 16 hours at 40°C to yield a polyurethane rubber having an impedance of about 1.50 M Rayl, an attenuation of 2MHz radiation of 2.8 dB/cm and a hardness of 31 IRHD. Repitition of this experiment using a curing cycle of 16 hours at 40°C (i.e. omitting the 1 hour at 100°C) yielded a rubber of similar attenuation (3.0 dB/cm), but the material was rather soft.

(c) Prepolymer (100g), T32/75 (200g) and, as catalyst, stannous octoate (0.1g) were heated for 1.5 hours at 100°C to yield a polyurethane rubber having an impedance 1.46 M Rayl, an attenuation of 2MHz radiation of 2.4 dB/cm and a hardness of 33 IRHD.

EXAMPLE 6

(a) To isophorone diisocyanate (3,39Kg) under nitrogen and stirred at 90 to 100°C was added over a period of 2 to 3 hours T32/75 (16.0Kg) preheated to 100 to 110°C. The temperature of the reaction mixture was maintained between 110 and 120°C during the addition and then allowed to rise slightly to 120 to 130°C for a further 6 hours. The prepolymer product had a free NCO content of 4.5%.

(b) A sample of the prepolymer so prepared (65.4g), T32/75 (120g) and, as catalyst dibutyltindilaurate (2.8g, 1.5% by weight) were heated for 24 hours at 40°C to yield a polyurethane rubber having an impedance of 1.50 M Rayl, an attenuation of 2 MHz radiation of 2.6 dB/cm and a hardness of 32 IRHD.

(c) The procedure of Example 6(b) was repeated with the exception of the addition of 0.06% by weight of nubian black B.T. and the resultant black polyurethane rubber had an impedance of 1.50 M Rayl, an attenuation of 2 MHz radiation of 2.4 dB/cm and a hardness of 32 IRHD.

EXAMPLE 7

A polyoxypropylene glycol of molecular weight 3700 and hydroxyl number 30

$$\left(\frac{\text{molecular weight}}{\text{hydroxyl number}} = 123\right)$$

commercially available from ICI Limited, under the code number F 3001, (50g) toluene diisocyanate (2.6g) and, as catalyst, stannous octoate (0.05g) were mixed, degassed and heated to 100°C for 40 hours. The resultant polurethane rubber which was very soft and tacky had an impedence of 1.57 M Rayl had an attenuation of 2MHz radiation of 2.5 dB/cm.

EXAMPLE 8

A polyether polyol (50g) having a molecular weight of 6000 and a hydroxyl number 28

$$\left(\frac{\text{molecular weight}}{\text{hydroxyl number}} = 214\right)$$

commercially available from ICI Limited under the code name R102 was reacted with isophorone diisocyanate (3.1g) at 100°C for 16 hours using as catalyst dibutyltindilaurate (0.8g) to yield a polyurethane rubber having an impedance of 1.48 M Rayl, an attenuation of 2 MHz radiation of 2.3 dB/cm, and a hardness of 32 IRHD.

EXAMPLE 9

A polyoxyproplene glycol of molecular weight 4000 and hydroxyl number 41.7

$$\left(\frac{\text{molecular weight}}{\text{hydroxyl number}} = 96\right)$$

commercially available from Dow Chemicals Limited under the code number CP4000 (500g) was added over one hour to isophorone diisocyanate (115g) with stirring under nitrogen and the resultant mixture heated to 120°C for 15 minutes whilst continuing to stir. A portion (100g) of the prepolymer produced by this procedure was heated to 100°C with CP4000 (160g) and, as catalyst, stannous octoate (0.1g) for 16 hours to yield a polyurethane rubber impedance 1.57 M Rayl and attenuation of 2MHz radiation of 3.9 dB/cm.

The rubbers produced by the procedures of Examples 1, 2, 4b, 5b, 5c and 6 are particularly suitable for casting into a stand-off unit of the form illustrated in Figure 1. The walls of the rectangular opening, 3, may be strengthened for example by the following procedure. A unit as illustrated in Figure 1 was inverted and portion 2 dipped in toluene to remove any traces of grease. It was then dipped in a solution prepared as described below and slowly removed therefrom at a rate of 5 inches per minute. This deposited a coating on the portion 2 which was first air dried for 30 minutes and then further dried in an oven at 100°C for an hour. The resulting coating, of approximately 10^{-3} inches thickness was found to add significantly to the mechanical strength of portion 2 without making any reduction in the properties of transmission of ultrasonic radiation. The coating solution was prepared as follows:

A polyester of molecular weight 1200 and hydroxyl number 90 was reacted with an excess of isophorone diisocyanate to give a prepolymer. A mixture of this prepolymer (500g) with trimethylol propane (27g) at 80°C was dissolved in methylethyl ketone (1500ml) and toluene (50ml), stannous octoate catalyst (5g) stirred in and the resultant solution allowed to cool to room temperature.

CLAIMS

1. An ultrasonic stand-off unit fabricated from a polyurethane rubber and having an attenuation of ultrasonic radiation of frequency 2 MHz of from 0.5 to 4.0 dB/cm and an acoustic impedance of from 1.45 to 1.6 M Rayles.

2. A unit according to Claim 1 having a hardness of from 15 to 50 IRHD.

3. A unit according to Claim 1 or Claim 2 which is substantially inert to silicone and paraffin lubricant.

4. A unit according to any one of Claims 1 to 3 which is optically substantially transparent.

5. A unit according to any one of Claim 1 to 4 having an attenuation of ultrasonic radiation of frequency 2 MHz of from 2.0 to 3.0 dB/cm.

6. A unit according to Claim 1 wherein said polyurethane rubber is formed by the reaction of a polyether polyol and a diisocyanate said polyether polyol having a chemical structure such that the ratio of molecular weight to hydroxyl number is at least 90.

7. A unit according to Claim 6 wherein said polyether polyol is a polyoxypropylene glycol of molecular weight between 3500 and 6000.

8. A unit according to Claim 6 or Claim 7 wherein substantially stoichmetric amounts of said polyether polyol and said isocyanate are used.

9. A unit according to Claim 8 wherein an initial reaction of said polyether polyol with excess of said isocyanate to form a prepolymer is followed by reaction of said prepolymer with a further quantity of said polyether polyol.

10. A unit according to Claim 9 wherein said prepolymer contains from 3.5% to 5.0% by weight of unreacted isocyanate groups.

11. A unit according to any one of Claims 6 to 10 wherein a catalyst such as 1,4-diazobicyclo (2,2,2) octane is used.

12. A unit according to Claim 9 or Claim 10 wherein dibutyltindilaurate is used as catalyst in an amount of from 1.2% to 2.1% by weight.

13. A unit according to Claim 6 wherein said polyurethane rubber is formed by a method substantially as hereinbefore described in any one of Examples 1 to 9.

14. A unit according to any one of the preceding Claims as hereinbefore described with reference to and as illustrated in the accompanying drawing.

15. An ultrasonic diagnostic apparatus comprising a source of ultrasonic radiation and a stand-off unit according to any one of the preceding Claims.

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